

Chemistry

Lecture 3

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Alkyl Halides

Outline:

Alkyl Halides/Halogenoalkanes:

- ✚ Classification of Alkyl halides
- ✚ Nomenclature
- ✚ Reactions
- ✚ Mechanism of nucleophilic substitution reaction S_N1 , S_N2 , E1 and E2 reaction

Alkyl Halides/Halogenoalkanes(Haloalkanes)

- General formula $C_nH_{2n+1}X$ (for one halogen atom)
- Most methyl halides are gases at room temperature
- Alkyl fluorides and alkyl chlorides mostly are lighter than water
- Alkyl bromides and alkyl iodides are heavier than water
- Alkyl halides prefer nucleophilic substitution reactions

Types:

Which one is monohaloalkane?

(a) CH_2Cl_2 (b) $CHCl_3$ (c) $CH_3CH_2CH_2Cl$ (d) CCl_4

- ◆ **Primary Alkyl Halides:** If carbon to which halogen atom is attached is further directly attached with one or no carbon atom.
- ◆ **Secondary Alkyl Halides:** If carbon to which halogen atom is attached is further directly attached with two carbon atoms.
- ◆ **Tertiary Alkyl Halides:** If carbon to which halogen atom is attached is further directly attached with three carbon atoms.

Which of the following is primary alkyl halide?

a) Iso-propyl halide (b) Sec.butyl halide (c) Ter.butyl chloride (d) Neo-pentyl halide

Common Names of Alkyl halides:

- ◆ Alkyl halide
like CH_3Cl is methyl chloride, C_2H_5Br is called ethyl bromide.

IUPAC Rules for Alkyl halides (Haloalkanes):

Selection of Chain:

- ⚙ Select the longest continuous carbon chain to halogen atom is attached directly.
- ⚙ If more than one chain is of same length, then select one with maximum no. of halogen atoms.
- ⚙ If no. halogen atoms is same, select one with maximum substituents and if substituents are also same, then select any.

Numbering:

- Start numbering from the end nearer to halogen atom and if halogen atom is at same distance from both ends, start numbering from end nearer to substituent.
- If substituent is also at same distance, then start numbering from either end.

Naming:

- Halogens are also treated as substituents while giving name.
Position of substituent-name of substituent alkane
- ♦ **Naming of Halogens:**
- If same halogens are present, use prefixes di, tri, tetra etc mentioning position for every substituent (no. of substituents = no. of positions).
- If different halogens are present, name them alphabetically.

Preparation:

Best Method from Alcohols

$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$
$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$
$C_2H_5OH + PCl_3 \rightarrow C_2H_5Cl + H_3PO_3$
$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

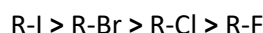
- Best method of preparation is from $SOCl_2$ /pyridine as the products are gases
- They are prepared from alkanes directly except iodide which are prepared using NaI/KI with RCl/RBr

Alkyl halides are considered to be very reactive compounds towards nucleophile because;

- (a) They have an electrophilic carbon
- (b) They have an electrophilic carbon and a good leaving group
- (c) They have an electrophilic carbon and a bad leaving group
- (d) They have a nucleophilic carbon and a good leaving group

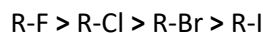
Reactivity:

♦ On basis of bond energy



R-I has longer bond length and breaks easily due to large size of iodine

♦ On basis of bond polarity



♦ On basis of experiments

Which statement is incorrect about reactivity of alkyl halides with respect to nucleophile?

- (a) Greater the bond energy of R-X, lesser the reactivity
- (b) Greater the bond polarity of R-X, lesser the reactivity
- (c) Greater the bond energy of R-X, smaller is the stability
- (d) Greater the E.N difference of R-X, greater is the stability

Which statement is incorrect about nucleophilic substitution reaction?

- (a) Incoming nucleophile must be stronger than the leaving one
- (b) Leaving nucleophile must be stronger than incoming nucleophile
- (c) Tertiary alkyl halides generally give SN_1
- (d) SN_2 is a single step reaction

Nucleophile and Electrophile

Nucleophile	Electrophile
Rich in electrons	Electron deficient
Donate electron pair to form bond	Accept electron pair to form bond
May carry lone pair	+ve or partial +ve (high charge density)
Lewis bases	Lewis acids

If an nucleophile is attacking reagent which one would be most reactive?

- (a) R-F (b) R-Cl (c) R-Br (d) R-I

Which is strong nucleophile?

a)NH₃(b) H₂O(c) HF(d) All are of equal strength

Negative: halide ions, OH ⁻ , R ⁻ , CN ⁻ , CH ₃ COO ⁻ , NH ₂ ⁻ , SH ⁻ , RO ⁻ etc. Neutral: H ₂ O, H ₂ S, NH ₃ , ROH, ROR, N ₂ H ₄ etc. Pi electrons: double, triple bonds, benzene ring.	Positive: Carbocation, acyl group, alkyl group, acetyl group, CH ₃ ⁺ , NO ₂ ⁺ etc
Nucleophilicity decreases across the period and increases down the group. CH ₃ ⁻ >NH ₂ ⁻ >OH ⁻ >F ⁻ (Period) NH ₃ >H ₂ O>HF F ⁻ <Cl ⁻ <Br ⁻ <I ⁻ (in Group)	Neutral: BF ₃ , SO ₃ , FeX ₃ , AlCl ₃ , BeCl ₂ , ZnCl ₂ etc.

Which one among the following is not a good leaving group?

(a)HSO₄⁻(b) OH⁻(c) Cl⁻(d) Br⁻

Leaving Group: An atom or group of atoms which departs with unshared pair of electrons when nucleophile attacks on substrate.

◆ **Good Leaving Groups:** HSO₄⁻, Cl⁻, Br⁻, I⁻ (I⁻ is good L.G and Nucleophile, also best L.G among them)

◆ **Poor Leaving Groups:** OH⁻, OR⁻, NH₂⁻

Good L.G ∝ Polarizability (size)

Good L.G ∝ $\frac{1}{\text{Electronegativity}}$

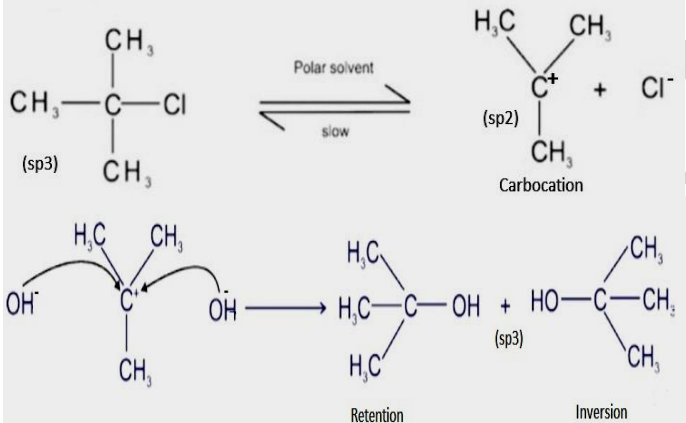
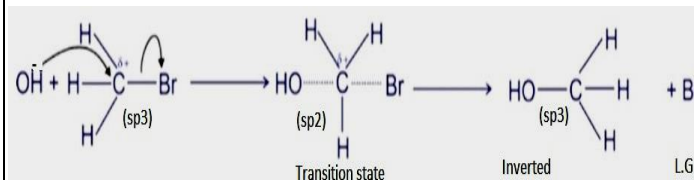
Reactions of Alkyl Halides and Mechanisms

Nucleophilic Substitution Reactions (S_N): Reactions in which halogen atom is replaced by another atom.

Occurs in presence of aqueous KOH.

An alkyl halide may be converted to alcohol by;

a)Addition(b) Substitution(c) Elimination(d) Rearrangement

S _N 1	S _N 2
 <p>What is the shape of Carbocation formed during SN1 mechanism? a)Linear(b) Square planar(c) Triangular planar (d) Tetrahedral</p>	 <p>The organic chloro compound which shows complete chemical inversion during SN2 reaction is; a)(C₂H₅)₂CHCl(b) (CH₃)₂CHCl(c) (CH₃)₃CCl(d) CH₃Cl</p>
Two step mechanism	One step mechanism
Nucleophile can attack from either side of Carbocation	Nucleophile attacks from opposite side of L.G
50 % inversion, 50 % retention in configuration	100% inversion in configuration
1 st step is slow and rate determining	Only step involved gives rate
Rate = k [Alkyl halide]	Rate = k [Alkyl halide][OH ⁻]
Molecularity = 1 Order = 1	Molecularity = 2 Order = 2
Favoured by polar solvent	Favoured by non polar solvent
Tertiary give S _N 1	Primary give S _N 2
Secondary in polar solvents	Secondary in non polar solvents
Reactivity order; 3° > 2° > 1° > CH ₃ -X(Never give S _N 1)	Reactivity order; CH ₃ -X > 1° > 2° > 3°

Which of the following is correct about SN2 reactions?

(a)Breakage of C-X and formation C-Nu bonds are simultaneous
 (b)Inversion of the configuration of the alkyl halide molecule
 (c)2nd order kinetics
 (d)All of these

Which of the following is correct about SN1 reactions?

(a)Retention and inversion of the configuration of the alkyl halide molecule
 (b)Unimolecular reactions
 (c)Reaction rate is a function of the [alkyl halide]
 (d)All of these

15. Whether an alkyl halide follows SN1 or SN2 mechanism depends on;
 (a) Steric hindrance (b) Inductive effect (e- donating effect) (c) Stability of carbocation (d) All

Which among CH₃X, R-CH₂-X, R₂CH-X, R₃C-X is most reactive towards SN1 reaction;

a) CH₃-X (b) R-CH₂-X (c) R₂CH-X (d) R₃C-X

Not depend on nature of attacking nucleophile	Strong nucleophile is required
Require good leaving group	Require good leaving group

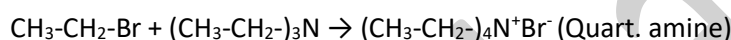
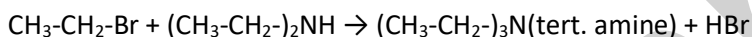
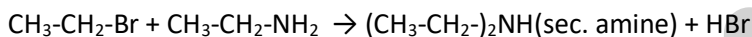
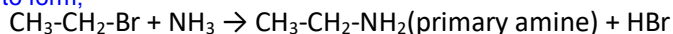
Neo-pentyl bromide refers to follow which mechanism during substitution reactions;
 (a) SN1 (b) SN2 (c) Both 'a' & 'b' (d) Neither 'a' & 'b'

Examples of S_N Reactions:

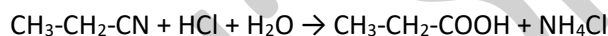
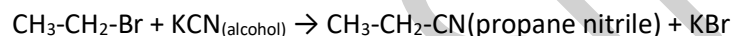
◆ With NH₃:

Ammonia reacts with excess of alkyl halide to form;

(a) pri. amine (b) sec. amine
 (c) tert. amine (d) Mixture of all of these



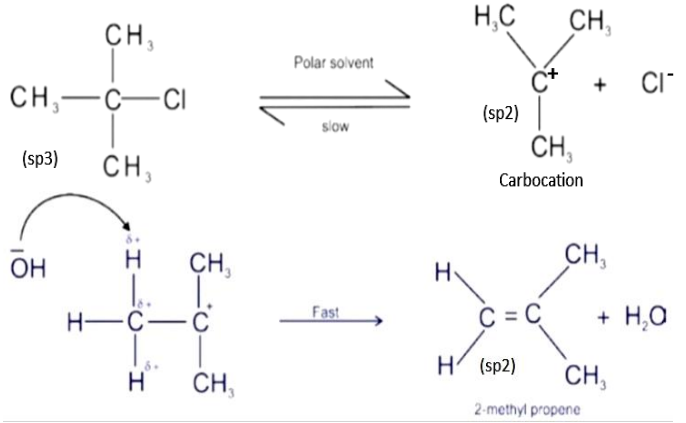
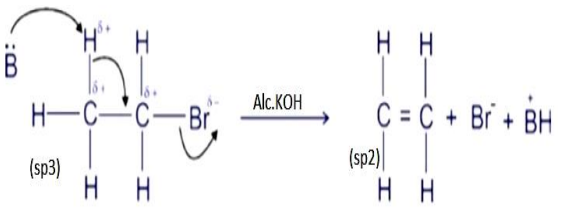
◆ With KCN:



- Which alkyl halides will produce ethane nitrile?
- Which acid can be produced from 1-chloro butane?

β-Elimination Reactions (E): Reactions in which β-hydrogen along with halogen is removed in the form of HX by the attack of nucleophile. Occurs in presence of alcoholic KOH

The mechanism involved in the reaction,
 $\text{KOH} + \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{KBr} + \text{H}_2\text{O}$
 a) SN1 (b) SN2 (c) E1 (d) E2

E1	E2
	
Two step mechanism	One step mechanism
Nucleophile can attack from either side of Carbocation	Nucleophile attacks from opposite side of L.G
1 st step is slow and rate determining	Only step involved gives rate
Rate = k [Alkyl halide]	Rate = k [Alkyl halide][OH ⁻]
Molecularity = 1 Order = 1	Molecularity = 2 Order = 2
Favoured by polar solvent	Favoured by non polar solvent

Elimination bimolecular reactions involve;
 (a) 1st order kinetics (b) 2nd order kinetics (c) 3rd order kinetics (d) zero order kinetics

In β-elimination the resulting product is;
 (a) Alcohol (b) Alkyl halide (c) Alkane (d) Alkene

β-elimination reactions are due to;
 (a) Attack of the incoming base/Nu on alpha hydrogen
 (b) Attack of the incoming base/Nu on beta hydrogen
 (c) Attack of the incoming base/Nu on alpha carbon
 (d) Attack of the incoming base/Nu on electrophilic carbon

(CH₃)₂CH-X in presence of polar solvent and strong base gives;
 (a) SN1 (b) SN2 (c) E2 (d) E1

Tertiary give E1	Primary give E2
Secondary in polar solvents	Secondary in non polar solvents
Reactivity order; 3° > 2° > 1°	Reactivity order; 1° > 2° > 3°
Strong base (relatively weaker than E2)	Strong base
Require good leaving group	Require good leaving group

The rate of E2 reaction depend on;
 (a) Concentration of substrate
 (b) Concentration of Nu/base
 (c) Concentration of substrate and Nu/base
 (d) Polarity of solvent

Comparison between S_N and E reactions:

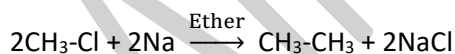
S _N Reactions	E Reactions
At low temperature	At high temperature
More polar conditions	Less polar conditions
Normally in aqueous conditions	Normally in alcoholic conditions
Steric hinderance does not favour	Steric hinderance favours
Both S _N 1 and E1 have 1 st steps same	

Some other Reactions of Alkyl Halides:

When two moles of ethyl bromide react with two moles of sodium metal in presence of ether, what will be formed?
 a) 2 moles of ethane (b) 1 mole of ethane (c) 2 moles of butane (d) 1 mole of butane

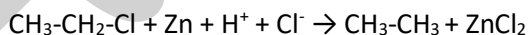
◆ Wurtz Synthesis:

- To prepare symmetrical alkanes
- Double no. of carbons in alkane produced than respective alkyl halide



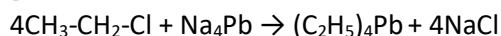
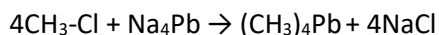
◆ Reduction of Alkyl Halides:

- To prepare alkanes
- Reduced with Zn dust in aqueous acid
- Same no. of carbons in alkane produced as of respective alkyl halide



◆ Reaction with Sodium Lead Alloy (Na₄Pb):

- To prepare anti knocking agents i.e. tetramethyl lead and tetraethyl lead



Importance of Halogenoalkanes

Chlorofluorocarbons (CFC'S)	Halothane	Teflon $-(CF_2-CF_2)_n-$	Chloroform (CHCl ₃)	Carbon tetrachloride (CCl ₄)
CCl ₂ F ₂ , CClF ₃	2-bromo-2-chloro-1,1,1-trifluoroethane	Polymer of the tetrafluoro-ethylene	Used as solvent	Used to create inert atmosphere
Used as refrigerants	Used as anesthetic	Used in corrosion proof parts of machinery	As the cleansing solvent	As the fire extinguisher
Used as the aerosol propellants	$\begin{array}{c} \text{F} \quad \text{Br} \\ \quad \\ \text{F}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{F} \quad \text{Cl} \end{array}$	Non stick coating of cooking pans	As a preservative for anatomical specimen	Used as solvent in halogenation of alkene/alkyne
		Used for coating of electrical wiring	As anesthetic Distinguish primary amines from others	